CONTININOUS TIME-OF-FLIGHT ION MASS SPECTROMETER

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ION MASS SPECTROMETER

FIELD OF THE INVENTION

10   The present invention generally relates to mass spectrometers, and, more specifically, relates to a time-of-flight ion mass spectrometer that can operate continuously. This invention was made with Government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

15   ## BACKGROUND OF THE INVENTION

Mass spectrometers are used extensively in the scientific community to measure and analyze the chemical compositions of substances. In general, a mass spectrometer is made up of a source of ions that are used to ionize neutral atoms or molecules from a solid, liquid or gaseous substance, a mass analyzer

20   that separates the ions in space or time according to their mass or their mass-per-charge ratio, and a detector. Several variations of mass spectrometers are available, such as magnetic sector mass spectrometers, quadrupole mass spectrometers, and time-of-flight mass spectrometers.

The magnetic sector mass spectrometer uses a magnetic field or

25   combined magnetic and electrostatic fields to measure the ion mass-per-charge ratio. In one type of magnetic sector geometry, {see A.O. Nier, *Review of Scientific Instruments*, Vol. 18 (1947) p. 398; L. Holmlid, *International Journal of Mass Spectrometry and Ion Physics*, Vol. 17 (1975) p. 403} only one mass-per-charge species is detected at any one time, so the magnetic field strength and, if

30   present, the electric field strength must be varied in order to obtain a mass spectrum comprising multiple mass-per-charge species. Major limitations on this type of mass spectrometer are the high mass of the magnet and the time that is required to scan the entire mass range one mass at a time.

Another type of magnetic sector mass spectrometer creates a

35   monoenergetic beam of ions, which are spatially dispersed according to mass-per-charge ratio, and which are focused onto an imaging plate {e.g., J. Mattauch and R. Herzog, *Zeitschrift fur Physik*, Vol. 89 (1934) p. 786}. While this type of

5   and R. Herzog, *Zeitschrift fur Physik*, Vol. 89 (1934) p. 786}. While this type of spectrometer can detect multiple mass-per-charge species can be detected simultaneously, the poor spatial resolution it provides limits its use to a narrow mass range.

    Quadrupole mass spectrometers utilize a mass filter having dynamic
10   electric fields between four electrodes {e.g., <u>Quadrupole Mass Spectrometer and its Applications</u>, ed. Peter H. Dawson (American Institute of Physics, New York, 1995)}. These fields are tailored to allow only one mass-per-charge ion to pass through the filter at a time. Major limitations of quadrupole mass spectrometers are the high mass of mass of the required magnet and the time required to scan
15   the entire mass range one mass at a time.

    Time-of-flight mass spectrometers (TOFMS) can detect ions over a wide mass range simultaneously {see W.C. Wiley and I.H. McLaren, *Rev. Sci. Instrum.*, Vol. 26 (1955) p. 1150; M. Guilhaus, *J. Mass Spectrom.*, Vol. 30 (1995) p. 1519}. Mass spectra are derived by measuring the times for individual ions to
20   traverse a known distance through an electrostatic field free region. In general, the mass of an ion is derived in TOFMS by measurement or knowledge of the energy, E, of an ion, measurement of the time, t_1, that an ion passes a fixed point in space, P_1, and measurement of the later time, t_2, that the ion passes a second point, P_2, in space located a distance, d, from P_1. Using an ion beam of known
25   energy-per-charge E/q, the time-of-flight (TOF) of the ion is $t_{TOF}=t_2-t_1$, and by the ion speed is $v=d/t_{TOF}$. Since $E=0.5\ mv^2$, the ion mass-per-charge m/q is represented by the following equation:

$$\frac{m}{q} = \frac{2Et^2{}_{TOF}}{qd^2}.$$
    10

    The mass-per-charge resolution, commonly referred to as the mass
30   resolving power of a mass spectrometer, is defined as:

$$\frac{\Delta m/q}{m/q} = \frac{\Delta E}{E} + 2\frac{\Delta t_{TOF}}{t_{TOF}} + 2\frac{\Delta d}{d},$$
    11

5   where ΔE, Δt_{TOF}, and Δd are the uncertainties in the knowledge or measurement of the ion's energy, E, time-of-flight, t_{TOF}, and distance of travel, d, respectively, in conventional time-of-flight spectrometers.

     In a gated TOFMS in which a narrow bunch of ions is periodically injected into the drift region, uncertainty in t_{TOF} may result, for example, from ambiguity in

10   the exact time that an ion entered the drift region due to the finite time, Δt_1, that the gate is "open," i.e. $\Delta t_1 \approx \Delta t_{TOF}$. The ratio of $\Delta t_{TOF}/t_{TOF}$ can be minimized by decreasing Δt_{TOF}, for example, by decreasing the time the gate is "open." This ratio can also be minimized by increasing t_{TOF}, for example, by increasing the distance, d, that an ion travels in the drift region. Often, a reflectron device is

15   used to increase the distance of travel without increasing the physical size of the drift region.

     Uncertainty in the distance of travel, d, can arise if the ion beam has a slight angular divergence so that ions travel slightly different paths, and, therefore, slightly different distances to the detector. The ratio of $\Delta d/d$ can be

20   minimized by employing a long drift region, a small detector, and a highly collimated ion beam.

     The uncertainty in the ion energy, E, may result from the initial spread of energies, ΔE, of ions emitted from the ion source. Therefore, ions are typically accelerated to an energy, E, that is much greater than ΔE.

25   A further limitation of conventional mass spectrometry lies in the fact that the source of ions is a separate component from the time-of-flight section of a spectrometer, and it requires significant resources. First, most ion sources are inherently inefficient, so that few atoms or molecules of a gaseous sample are ionized, thereby requiring a large volume of sample and, in order to maintain a

30   proper vacuum, a large vacuum pumping capacity. Second, the ion source typically generates a continuous ion beam that is gated periodically, creating an inefficient condition in which sample material and electrical energy are wasted during the time the gate is "closed." Third, ions have to be transported from the ion source to the time-of-flight section, requiring, among other things,

5   electrostatic acceleration, steering and focusing. Fourth, typical ion sources introduce a significant spread in energy of the ions so that the ions must be substantially accelerated to minimize the effect of this energy spread on the mass resolving power. Finally, having an ion source separate from the drift region creates an apparatus having large mass and volume.

10   Still another problem with conventional time-of-flight mass spectrometers is that ions must be localized in space at time t_1 in order to minimize Δd and therefore, minimize the mass resolving power. Typically, time t_1 corresponds to the time that the ion is located at the entrance to the drift region.

In addition to these limitations that impact the mass resolving power of
15   prior art TOFMS, an important further limitation is the intrinsically low duty cycle associated with the gating process in which a group of ions briefly is admitted at time t_1 into the drift region. The time that must elapse before another group of ions can be admitted is determined by the time required for the heaviest, and therefore the slowest, ion, admitted at time t_1, to reach the detector. This
20   generally long period is necessary to prevent overlap of mass spectra, which are accumulated each gating period. Although sophisticated techniques have been developed in attempts to improve this limitation, the duty cycle of prior art TOFMS is still much less than unity.

One method of attempting overcome this limitation in TOFMS utilizes a
25   thin foil located at the entrance to the drift region. A sample ion having sufficient energy to traverse the foil will continue to the "stop" detector. Secondary electrons generated by the interaction of the sample ion with the foil are detected, and provide a measurement of the time t_1 that the ion entered the drift region. However, this method is not without its own limitations. These limitations
30   include the requirement that the incident ion have sufficient energy to transit the foil, the energy degradation of the sample ion due to interaction with the foil, and the angular scattering of the sample ion due also to its interaction with the foil.

The present invention solves these problems of the prior art by continuously ionizing sample atoms or molecules that are initially at rest inside a

5 drift region having an electric field. The secondary electron that is created by the ionization event is detected to provide the time t_1, and the detection of the ion at a "stop" detector provides the stop time t_2.

SUMMARY OF THE INVENTION

In order to achieve the objects and purposes of the present invention, and
10 in accordance with its objectives, a time-of-flight ion mass spectrometer comprises an evacuated enclosure, with means for generating an electric field located in the evacuated enclosure, and means for injecting a sample material into the electric field. A source of continuous ionizing radiation injects ionizing radiation into the electric field to ionize atoms or molecules of
15 the sample material, and timing means for determining time elapsed between arrival of a secondary electron having a particular energy out of the ionized atoms or molecules at a first predetermined location and arrival of a sample ion having a particular energy out of the ionized atoms or molecules at a second predetermined location.

20

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawing, which is incorporated in and forms a part of the specification, illustrates an embodiment of the present invention and, together with the description, serves to explain the principles of the invention. In the
25 drawing:

FIGURE 1 is a schematic illustration of an embodiment of the present invention showing the elements of the invention and its operation with a static electric field.

FIGURE 2 is a schematic illustration of another embodiment of the present
30 invention in which one method of introducing a linear electric field.

FIGURE 3 is a schematic illustration of still another embodiment of the present invention in which a thin foil is installed at each end of the drift region.

5   FIGURE 4 is a schematic illustration of still another embodiment of the present invention in which the energy of the secondary electron and the energy of the ion are measured.

DETAILED DESCRIPTION

The present invention continuously ionizes sample atoms or molecules

10   within a drift region having an electric field of magnitude $\varepsilon(z)$, aligned coaxially with the central z-axis of a drift region. The electric field accelerates the secondary electrons toward a first detector, and the generated ions toward a second detector. The invention provides high mass resolving power, smaller resource requirements in such areas as mass, power, volume, and pumping

15   capacity, a high efficiency, since nearly every ionization event is detected, and elimination of the prior art requirement that the location of an ion at time t_1 must be known in order to measure its time-of-flight in the drift region. The invention can be understood more easily through reference to the drawing.

Referring to Figure 1, there can be seen the time-of-flight mass

20   spectrometer **10** of the present invention resides inside evacuated chamber **11**. The gaseous sample to be investigated is introduced into drift region **12** by sample inlet **13**. Alternatively, a solid sample could be introduced, for example, at the surface of an electrode placed in drift region **12**. As shown, a static electric field exists between start detector **17** and stop detector **16** due to the difference

25   in voltage between V_1 and V_2, with V_1 being negative with respect to V_2.

The general equation governing the motion of an ion in a static electric field is:

$$m\frac{d^2z}{dt^2} = q\varepsilon(z) \quad ,$$

12

which can be solved analytically or numerically depending on the functional form

30   of $\varepsilon(z)$. For a sample ion initially at rest, the solution of Equation 11 provides the mass-per-charge of the sample ion if the time-of-flight, t_{TOF}, distance of travel, d, and electric field, $\varepsilon(z)$, are known.

5   If the electric field created by the difference in potential between V_1 and V_2 is constant across the drift region, as it is in one embodiment of the present invention (i.e., $\varepsilon(z) = \varepsilon_0$), and the ionization event occurs at a known distance from stop detector **16**, the mass-per-charge of an ion initially at rest is:

$$t_{TOF} = \left(\frac{2md}{q\varepsilon_0} \right)^{1/2} .$$
13

10   Under the initial conditions that stop detector **16** is located at $z = 0$, and that the ion is created at rest at a distance of $z = d$ from stop detector **16**, the time-of-flight of the ion according to Equation 12 is:

$$\frac{m}{q} = \frac{\varepsilon_0 \, t_{TOF}^2}{2\,d} .$$
14

Knowledge of the distance of travel, d, generally requires that the
15   ionization event occur at a fixed, known distance from stop detector **16**. This can be achieved by using a continuous ionizing radiation source **19** whose ionizing particles are confined to a thin plane having a thickness, g, oriented perpendicular to the z-axis. However, the mass resolving power of the present invention is dependent on g/d, which can be minimized by minimizing g.

20   Continuous ionizing radiation source **19** ionizes sample atoms or molecules and creates a secondary electron that is accelerated to start detector where it is detected at time, t_1. The ionized atom or molecule also is accelerated by the electric field, but toward stop detector **16**, where the ionized atom or molecule is detected at time, t_2. The time-of-flight of the secondary electron from
25   the ionization event to the start detection is much shorter than the time-of-flight of the ion from the ionization event to the stop detector, so the difference in times, $t_2 - t_1$, corresponds to the time-of-flight of the ionized atom or molecule over the distance that it travels from the time it was ionized to the time it is detected at stop detector **16**.

30   An ionized sample atom or molecule is considered to be initially at rest in the z direction if its initial energy in the z-direction is much less than the energy to which the ion is accelerated in drift region **12**. It is well known to those having

5   skill in this art, that the mean kinetic energy of a gaseous atom or molecule is 1.5 kT, where k is the Boltzman constant, and T is the temperature of the gas. At room temperature (approximately 300 K), the mean energy is approximately 0.04 eV. Therefore, an ionized sample atom or molecule can be at rest if the energy to which it is accelerated by the linear electric field in drift region **12** is much

10   greater approximately 0.04 eV. For example, a typical acceleration by the electric field would be several kilovolts, so an ion can be considered to initially at rest.

       Another embodiment of the present invention utilizes an electric field that linearly increases in magnitude along the z-axis in drift region **12** from stop

15   detector **16** to start detector **17**, as is shown in Figure 2. In this embodiment, the electric field is defined by $\varepsilon(z) = kz$, where k is a constant that depends only on the electromechanical configuration of drift region **12**. Assuming that a sample ion starts from a rest condition in drift region **12**, the solution of Equation 12 using this electric field will yield the time-of-flight (and therefore the mass-per-charge)

20   of a sample ion that is independent of the distance of travel, d, of the sample ion in drift region **12**. This eliminates the requirement that continuous ionizing radiation source **19** emit ionizing radiation that is confined to a plane perpendicular to the z-axis, and allows the ionizing radiation to be spatially broad in the z-direction.

25   In this embodiment of the present invention, concentric electrically conductive rings **14** surround drift region **12**, and are connected to resistors **15** that are connected between voltage V_1 and voltage V_2, as shown, again with V_1 negative with respect to V_2. Also as shown, V_1 is connected to stop detector **16**, and V_2 is connected to start detector **17** at the opposite end of drift region **12**.

30   This arrangement provides the electric field in drift region **12** that is required by this embodiment of the present invention. The values of resistors **15** are selected to generate the linear electric field along the central axis of drift region **12**. Generally, the values of resistors **15** increase quadratically from stop

5   detector **16** (V_1) to start detector **17** (V_2) for the case of a cylindrical drift region
12.

The electric field created by V_1 and V_2 across resistors **15** and
concentric rings **14** is coaxial about central axis **18** (the z axis), and has a
magnitude, $\varepsilon(z)$, normal to stop detector **16**, as shown in U.S. Patent No.

10   5,168,158, issued December, 1992, to McComas et al. Although concentric rings
14 and resistors **15** effectively provide the electric field for this embodiment of the
present invention using a linear electric field, other methods can be used. For
example, a dielectric cylinder could surround drift region **12**, and have a resistive
coating applied whose resistance varies with the distance from stop detector **16**.

15   Another electric field arrangement could involve appropriately shaped grids at
stop detector **16** (V_1) and at start detector **17** (V_2) (see D.C. Hamilton et al., New
high resolution electrostatic ion mass analyzer using time-of flight, Rev. Sci.
Instrum. Vol. 61 (1990) 3104-3106). It is also possible that combinations of these
methods could be used. Any method of effectively producing, in this

20   embodiment, a linear electric field within drift region **12** could be used with this
embodiment of the present invention.

Another embodiment of the present invention is illustrated in Figure 3,
where thin foils **16a** and **17a** are shown in place in front of stop detector **16** and
start detector **17**, respectively. Ions and secondary electrons associated with the

25   ionization event pass through foils **16a**, and **17a** to stop detector **16** and to start
detector **17**. Thin foils **16a**, **17a** allow the pressure in drift region **12** to be
maintained at a higher level than the operating pressure of start detector **16** and
stop detector **17**. This pressure differential also allows a greater amount of
sample atoms or molecules in drift region **12**, providing a higher ionization

30   probability per ionizing radiation particle from continuous ionization radiation
source **19**. It should be noted, however, that the output of sample inlet **13** must
be sufficiently low so that the inverse of the ionization rate, which equals the
average time between discrete ionization events, is much longer than the time-of-
flight of sample ions in drift region **12** in order to reduce the ambiguity introduced

5   from multiple signals from start detector **17** or stop detector **16** when two or more

ions are ionized nearly simultaneously.

Another embodiment of the present invention is illustrated in Figure 4. In

this embodiment, the energy of a secondary electron is measured using

electrostatic energy analyzer **20**. Since an ion and its secondary electron are

10   formed initially at rest, or nearly at rest, and are accelerated through a known

electric field, the energy of the electron at start detector **17**, and the energy of the

ion at stop detector **16** each provide information of the distance in the z-direction

that the initial ionization event occurred. Therefore, measurement of the energy

of the secondary electron, the energy of the ion, or both the energy of the

15   electron and the energy of the ion allows determination of the distance of travel,

d, of the ion from its formation to stop detector **16**. Measurement of the electron

energy is the preferred embodiment because the time for an electron to traverse

the additional path length required for energy measurement is much shorter than,

and therefore insignificant relative to, the time-of-flight of the ion.

20   Measurement of the energy of an ion or electron by electrostatic energy

analyzer **20** may be performed by means of a deflector-type electrostatic

analyzer or mirror-type electrostatic analyzer {see D. Roy and R.P. Harkness,

Reports on Progress in Physics, Vol. 53 (1990) p. 1621} and located as shown

near start detector **17**. To represent electrostatic energy analyzer **20** in Figure 4,

25   curvilinear plates **20a**, **20b** are shown connected to biasing voltages V_3 and V_4.

If desired, another electrostatic energy analyzer **21** can be located near stop

detector **16**. As shown, curvilinear plates **21a**, **21b** connected to biasing voltages

V_5 and V_6. According to the desired application of the present invention, either

electrostatic energy analyzer **20** or electrostatic energy analyzer **21** could be

30   used singly, or both electrostatic energy analyzer **20** and electrostatic energy

analyzer **21** can be used together.

In this embodiment, it is necessary to connect voltages V_1 and V_2 to

electrodes **22** and **23**, which define an aperture to allow secondary electrons and

sample ions to pass through. One important advantage of this embodiment is

5   that the ionizing radiation from continuous ionizing radiation source **19** can be

spatially broad in the z-direction.

For all embodiments of the present invention, stop detector **16** and start

detector **17** can be any effective single particle detectors that can measure the

time the sample ion strikes stop detector **16**, and the secondary electron strikes

10   start detector **17** with time accuracy much less the ion's TOF in drift region **12**.

Appropriate detectors for stop detector **16** and start detector **17** include

microchannel plate detectors or channel electron multiplier detectors that would

detect ionized sample atoms or molecules and secondary electrons that have

been accelerated through drift region **12**, and output a signal indicating that

15   detection.

Continuous ionizing radiation source **19** emits continuous ionizing

radiation into drift region **12** where it ionizes atoms or molecules of the gas

sample of interest. Continuous ionizing radiation source **19** can emit any

effective ionizing radiation, such as photons, electrons, or ions, and could be a

20   laser, a source of electrons, or a source of ions.

Those with skill in this art recognize that the invention requires a power

supply to provide the necessary potential differences required for V_1 and V_2,

where V_2 is biased negatively with respect to V_1, to produce the necessary

electric field, and to power pulsed ionizing radiation source **19**. Additionally,

25   power is required to be provided for the operation of stop detector **16** and start

detector **17**.

As has been explained, the present invention ionizes the sample atoms or

molecules inside drift region **12**, not in some external ion source. This allows the

invention to be inherently compact, allowing the invention to provide TOFMS

30   apparatus that has a small volume and mass, and that requires reduced power

resources. The ionization of sample atoms or molecules inside drift region **12**

also allows the present invention to accelerate the ions from a condition of near

rest independent of the ion's position within drift region **12**. This allows, in one

5   embodiment, use of a spatially broad continuous ionizing radiation source **19** that
is efficient and requires little or no steering, collimation or focusing.

In the present invention, the sample ion is formed when the sample atom
or molecule is approximately at rest, and the time-of-flight of the sample ion in
drift region **12**, in one embodiment, is independent of the location at which the

10   sample ion was formed. Therefore, the mass resolving power of the sample ion
is dependent only on the initial ion energy relative to the energy to which it is
accelerated and the accuracy of the time-of-flight measurement, which includes,
for example, the timing accuracy of the time-of-flight measurement electronics.

The present invention requires only a small volume of sample material

15   because most ions from sample atoms or molecules are detected. This is in
contrast to prior art mass spectrometers, where few ions are extracted from the
ion source to form an ion beam or ions that are extracted from the ion source and
comprise the ion beam are removed from the ion beam by, among other things,
collimating slits, and while the gate is "closed." Additionally, due to the smaller

20   volume of the present invention, the pumping requirements for evacuation of
evacuated chamber **11** is reduced, allowing use of a smaller vacuum pump.

Finally, the present invention requires lower voltage differences across
drift region **12**. Since a sample atom or molecule is ionized while it is at thermal
energies of approximately 0.04 eV at 300 K, the calculated mass-per-charge of

25   the ion is dependent on knowledge accuracy of the ion's energy relative to its
accelerated energy as it traverses drift region **12**. Because the spread in the
initial energies of the sample ions is small, the acceleration voltage (V_1-V_2) does
not have to be high. To put this into perspective, it should be noted that prior art
linear ion mass spectrometers have energy spreads that typically range from 2

30   eV to 40 eV, which requires acceleration of the sample ions to a high energy in
order to remove the uncertainty of the energies of the sample ions. In one
embodiment of the present invention, a single applied voltage (except for the
signal electronics) could be applied both as the bias for stop detector **16** and start

5 detector **17** and for the voltage V_1 - V_2 between stop detector **16** and start
detector **17**.

The foregoing description of the invention has been presented for
purposes of illustration and description and is not intended to be exhaustive or to
limit the invention to the precise form disclosed, and obviously many

10 modifications and variations are possible in light of the above teaching. The
embodiments were chosen and described in order to best explain the principles
of the invention and its practical application to thereby enable others skilled in the
art to best utilize the invention in various embodiments and with various
modifications as are suited to the particular use contemplated. It is intended that

15 the scope of the invention be defined by the claims appended hereto.